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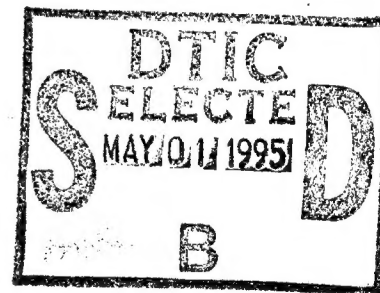
Evaluation of Halon Alternatives in Inerting Experiments

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13. ABSTRACT (Maximum 200 words) <p>Inerting experiments were conducted in a 20-liter stainless steel chamber. Eight potential Halon 1301 replacement agents were used to inert butane-air mixtures. The agents were ranked on the amount required to completely inert the system and on their tendencies to form hydrogen fluoride. A specific ion electrode was used to determine the amount of hydrogen fluoride formed when less than the amount of agent required for complete inertion was used in an experiment.</p> <p>The two iodine-containing agents, perfluoroethyl iodide and perfluoromethyl iodide, were superior to the other potential replacement agents in that less concentration was required for inertion and less hydrogen fluoride formed than with the others. The ability of perfluoroethyl iodide and perfluoromethyl iodide, which are chemical fire-extinguishing agents, to act as inerting agents is attributed to the ease of breaking of the relatively weak (ca. 57 kcal/mole) carbon to iodine bond at low temperatures. This enabled the iodine-containing agents to act as energy-absorbing agents, which is important in preventing ignition of fuel-air-agent mixtures.</p>				
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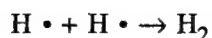
1. INTRODUCTION

The quest for replacements for the halon fire-extinguishing agents has led to several different classes of chemical compounds. One class, called perfluorocarbons (PFCs), may possibly be useful as halon replacements. The PFCs are attractive because they fulfill several requirements for acceptable halon replacements—zero ozone depletion potential (ODP), very low toxicity, and good physical properties (boiling points, freezing points, and densities). However, the PFCs are not expected to be as efficient as halon in extinguishing fires, since the PFCs are not able to act as chemical fire-extinguishing agents.

Materials are said to be chemical fire-extinguishing agents if they react to remove active chemical species (free radicals) from the flame. The removal of active species must be catalytic, with a given agent molecule being capable of destroying several active free radicals. A one-to-one removal (one agent molecule removing one free radical) does not qualify the agent as a chemical agent. Thus, in the case of Halon 1301,



adding (2), (3), and (4) gives



Hydrogen atoms, essential to flame chemistry, are forced to combine, yielding the much less reactive H_2 molecule. The HBr (hydrogen bromide) catalytically causes this combination of hydrogen atoms. Since HBr is not consumed, it can be responsible for the removal of many hydrogen atoms.

In the case of a PFC, perfluorobutane (C_4F_{10}),



the H to F bond is too strong (135 kcal/mole) to be broken by reaction with a hydrogen atom (Finnerty and Dehn 1994). Thus, HF (hydrogen fluoride), which does not cause catalytic removal of hydrogen atoms, is a final product.

The PFCs act primarily as physical agents, removing heat from the flame zone, lowering the flame temperature until extinguishment occurs. The lack of a bromine atom in the molecule means that the PFCs are not efficient chemical fire-extinguishing agents. Reliance on a physical heat-removing mechanism means that a higher concentration is required than is needed with halon and there is an expected longer time required to extinguish fires. Therefore, it follows that there should be a greater amount of pyrolysis of the PFCs during extinguishment than was found with halons. Indeed, it has been reported that more HF is produced when PFC agents are used than when halons are used to extinguish fires (Sheinson et al. 1994).

It is not obvious, however, that there should be an excess of HF production when PFCs are used in inerting scenarios, as distinguished from fire-extinguishing scenarios. If enough PFC is present in a fuel-air mixture before ignition occurs, the ignition hot spot (kernel) may be quenched virtually immediately due to heat extraction from the ignition kernel (Finnerty and Dehn 1994). Very little chemical reaction should occur, so very little HF should be formed. If this is true, PFCs can be very useful as inerting agents, but may pose toxic product problems when used to extinguish large fires.

Figure 1a is a representation of what occurs when an ignition source is brought into contact with a fuel-air mixture. The mixture explodes, and, if conditions of availability of fuel vapors and air are met, a sustained fire commences.

Figure 1b is a representation of what occurs when an ignition source is brought into contact with a fuel-air-heat absorbing agent mixture. The ignition process fails because heat is removed from the ignition kernel so rapidly, that the temperature falls below the minimum required for growth into an explosion. The small ignition kernel has a high surface-to-volume ratio. Heat is removed from the kernel at the surface. Heat is generated in the volume of the kernel; therefore, at ignition, the kernel is at the least favorable conditions for growth. Adding a heat-absorbing material to the fuel-air mixture increases the heat loss to the surroundings at the surface of the kernel. There is no increase in heat generation; therefore the temperature of the ignition kernel falls. If sufficient heat-absorbing material is present in the fuel-air mixture, the ignition process fails.

Figure 1c is particularly interesting. It depicts the situation in which an agent that functions by a chemical mechanism is added to a fuel-air mixture. If an ignition source is brought into contact with the mixture, ignition does indeed occur. However, there is no sustained fire, even if there is an available supply of fuel and air (Finnerty and Dehn 1994).

The chemical agent, which usually contains at least one bromine atom, is not efficient in absorbing heat well enough to prevent ignition. However, once ignition occurs, the chemical agent quickly quenches the fire. Hydrogen bromide is formed and is an efficient agent to remove free radicals from the flame. Therefore, even with available fuel and air, the flame is quenched.

The chemical agent does not become efficient until a flame is present, then the agent quickly quenches it. But the chemical agent will allow ignition to occur. To prevent ignition while using a chemical agent, enough agent must be used so that its heat-absorbing characteristic become important.

A class of non-bromine-containing compounds that may act as chemical fire-extinguishing agents is the iodine-containing chemicals. Data going back to the original Purdue work, sponsored by the Army after World War II, indicates that iodine-containing materials are approximately as effective as bromine-containing materials in extinguishing fires (Purdue 1950). High cost and concerns about toxicity, in addition to the effectiveness of the bromine agents, caused a neglect of iodine chemicals. Iodine agents became interesting when production of bromine agents was banned (U. S. House of Representatives 1990). The availability of compounds of fluorine, carbon, and iodine has given hope for a low toxicity iodine agent. Both environmental and toxological assessments of iodine agents are proceeding rapidly, although not yet completed. Of prime environmental concern is the ODP of perfluoroiodine agents.

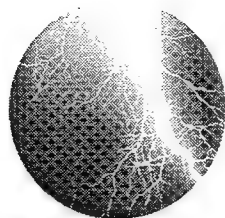
2. EXPERIMENTAL

2.1 Agents. The chemicals shown in Table 1 were utilized in inerting scenarios. The agents were premixed with butane (fuel) and air before ignition was attempted. They represent several classes of compounds which are being pursued as potential halon replacement agents, in addition to Halon 1301 itself.

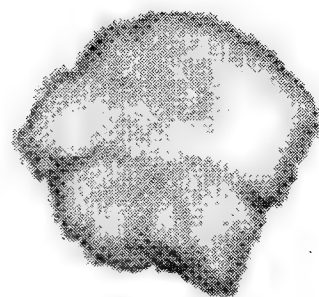
2.2 Apparatus. Inerting experiments were conducted using a 20-liter stainless steel chamber (Figure 2). With a stainless steel gasket in place and all bolts secured, the chamber is rated at a maximum



AIR plus FUEL



IGNITION SOURCE

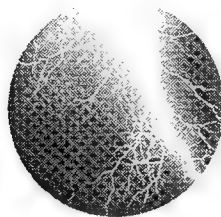


**FIREBALL
AND
SUSTAINED FIRE**

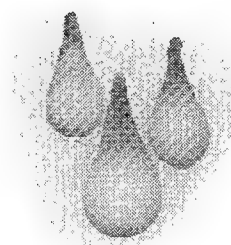
(a) No fire extinguishing agent present.



**AIR plus FUEL
HEAT ABSORBING
FIRE EXTINGUISHING
MATERIAL**



IGNITION SOURCE

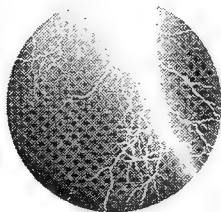


FIRE OUT

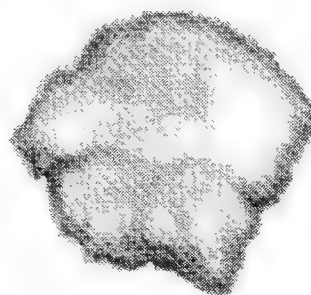
(b) In presence of a heat absorbing fire extinguishing agent.



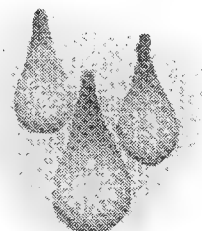
**AIR plus FUEL
plus CHEMICAL
FIRE EXTINGUISHING
MATERIAL**



IGNITION SOURCE



FIREBALL



FIRE OUT

(c) In presence of a chemically acting fire extinguishing agent.

Figure 1. Ignition of fuel-air mixture.

Table 1. Inerting Agents

Perfluorobutane
Perfluoroheptane
Perfluoromethylcyclohexane
Perfluoro - 2 - butyltetrahydrofuran
FE 232 (1,1,1 - Trifluoro - 2,2 - dichloroethane)
1,1 - Difluoro - 2 - bromoethylene
Halon 1301 (Trifluoromethylbromide)
Perfluoroethyl Iodide
Perfluoromethyl Iodide

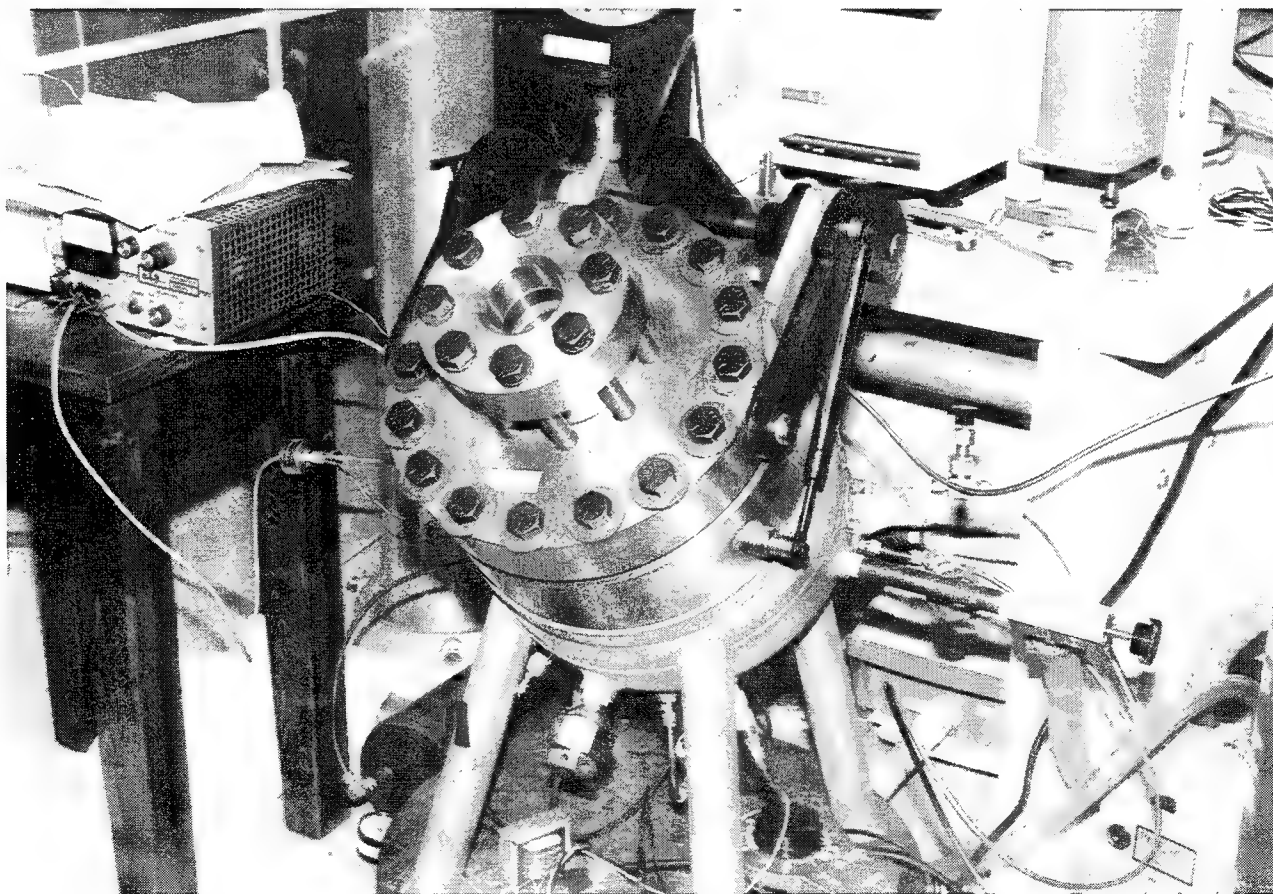


Figure 2. The 20-liter stainless steel chamber.

safe pressure of 10.2 MPa (1,500 psi). Multiple threaded openings into the chamber allow electrical pass throughs, valves, and pressure gauges to be used with the chamber.

Since applications of this work will be to Army combat vehicles, all tests were conducted at an initial total pressure of 0.1 MPa (1 atmosphere). Measured amounts of fuel (butane) and an inerting agent were placed in the 20-liter chamber. Make-up air was then added to ambient pressure. Ignition was accomplished using a 40-J exploding 0.008-mm-diameter nichrome wire. Any pressure spike was recorded. In some cases the atmosphere in the chamber was analyzed for any HF produced by the fluorine-containing agents with the flame. No attempt was made to analyze for any hydrogen iodide or hydrogen bromide which may have been formed from the iodine or bromine-containing agents.

2.3 Procedure for a Typical Run. A length of 0.008-mm-diameter nichrome wire was wound on a Teflon fitting originally intended for 6-mm-diameter tubing. Clamps connected to electrical pass throughs in the chamber wall were used to make contact with the wire. The cover of the stainless steel chamber was bolted shut. A vacuum pump was used to evacuate the chamber to a vacuum of 0.1 kPa (1 torr). The desired pressure of butane was added and the value was read from a digital pressure meter (0 to 1,000 torr). The pressure was also recorded on chart recorder paper. In the case of gaseous agents, the desired pressure of fire suppression agent was then added. Its value was obtained in the same way that the butane pressure was obtained. Air was added to atmospheric pressure and all valves were closed. The power supply was activated and the chart recorder was set to run. The power supply was then fired to explode the nichrome wire, causing ignition. The pressure pulse was read from the chart recorder paper. The gases in the chamber could then be analyzed for HF formation.

When liquid agents were used, the desired volume of agent was placed in a graduated cylinder. A Teflon tube, connected to one of the valves threaded into the chamber, was inserted into the graduated cylinder. When it was time to add the agent to the chamber, the valve was opened. Since the chamber was at a pressure well below atmospheric, the agent was drawn into the chamber where it flash evaporated. Air then entered the chamber through the Teflon tube until the total pressure was atmospheric. The valve was then closed. The ignition process was then carried out using the exploding nichrome wire. Analysis of HF could then be performed.

2.4 Analysis of HF. The basic method of HF analysis utilized a specific ion electrode that responded to fluoride ion concentration in aqueous solution. Under the proper pH conditions, the electrical output of this electrode is not influenced by any bromide or iodide which might be present.

Calibration of the fluoride concentration was carried out according to the instructions received from the supplier of the electrode (Omega Engineering). The resulting calibration chart is presented in Figure 3. The fluoride concentration in Figure 3 refers to the solution into which the specific ion electrode (and a reference electrode) is placed.

Any HF which was formed during an experiment was collected by extracting the gases from the stainless steel chamber and bubbling them through a gas washing bottle which contained a solution of potassium hydroxide in water.* The number of moles of potassium hydroxide in the solution was at least 2.7 times the maximum amount of HF which was anticipated for any experiment (20,000 ppm).

A Teflon tube was used to connect the output of a stainless steel valve, which was threaded into the chamber, with the input of the gas washing bottle. The output of the gas washing bottle was connected, via another Teflon tube, to the input of a diaphragm pump. The output of the pump, after passing through a gas flow measuring device, was returned to the stainless steel chamber via another Teflon tube. The gas flow rate was 2-liters per minute. Collection was carried out for 30 min. Thus, three volumes worth of the chamber were bubbled through the gas washing bottle.

After collection, 10 ml of the solution was removed by a pipette and diluted with 90 ml of a potassium acetate-acetic acid buffer. This ensured the proper pH and a constant ionic strength of the final solution into which the measuring electrode (and a reference electrode) was placed. The voltage of the cell thus formed was read on a digital pH-millivolt meter. The concentration of fluoride ion was determined from the previously established calibration graph for fluoride ion. The total amount of fluoride collected was easily calculated, as was the original concentration of HF in the 20-liter chamber. As a check, for several experiments, two gas washing bottles were used in series. The amount of fluoride collected in the second bottle was only about 3% of the amount collected in the first bottle. Since it was estimated that the values of the concentration of HF, as determined by this method, were accurate at best

*6.0 g KOH in 400 ml of solution.

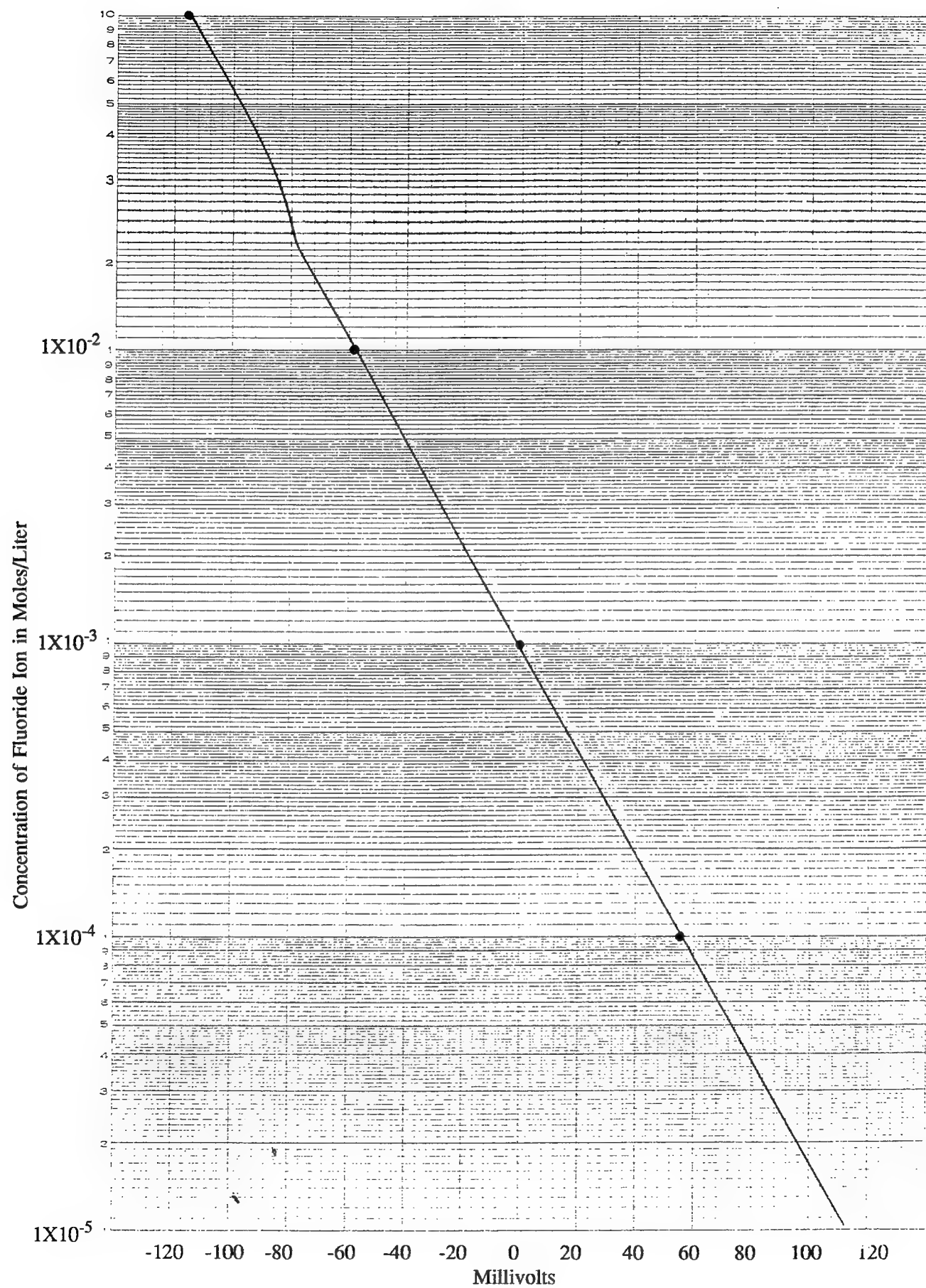


Figure 3. Voltage of fluoride specific ion electrode vs. concentration of fluoride ion in buffered solution.

to only about 3% at high HF concentrations and about 6.5% at low HF concentrations, no corrections were made to the calculated concentrations of HF. It was also found that a clean stainless steel surface inside the chamber gave lower HF values than a surface coated with carbonaceous material.

The original concentration of HF in the chamber (at STP conditions) was calculated knowing the concentration, C, in the final measuring solution.

$$\begin{aligned} \text{ppm HF} &= C \frac{\text{moles}}{1,000 \text{ ml}} \times \left[\frac{90 \text{ ml} + 10 \text{ ml}}{10 \text{ ml}} \right] \times \frac{400 \text{ ml} \times 10^6 \text{ ppm}}{0.818 \text{ mole}} \\ &= C \times 4.89 \times 10^6 \text{ ppm} \end{aligned}$$

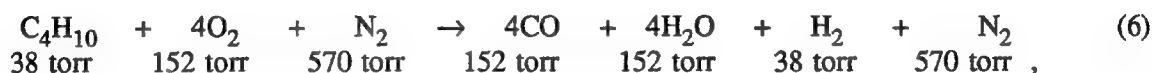
Therefore the voltage from the fluoride electrode (and reference electrode) was converted to solution concentration, C, using Figure 3. The concentration, C, was then multiplied by the factor 4.89×10^6 to obtain the concentration of HF, in ppm, in the chamber. The relationship of cell voltage and HF concentration in the chamber is given in Table 2.

Table 2. Fluoride Ion Cell Voltage vs. HF Concentration in 20-liter Chamber

Electrode Reading (mv)	Concentration of HF (ppm)	Electrode Reading (mv)	Concentration of HF (ppm)
+ 110	56	+ 30	1,370
+ 100	86	+ 20	2,078
+ 90	126	+ 10	3,179
+ 80	186	0	4,690
+ 70	264	- 10	7,091
+ 60	420	- 20	10,513
+ 50	587	- 30	15,648
+ 40	929	- 40	23,472

3. RESULTS

Several compounds were screened for their ability to act as-inerting agents for butane-air mixtures. The compounds were chosen largely on the basis of classes of potential halon replacement agents they represented and on availability. The testing was done at butane pressures of 38 torr and 30 torr. Even the 30-torr butane mixture with air to a total pressure of 1 atmosphere represents a fuel-rich mixture (based on CO₂ and H₂O as final products). Combustion of the 38-torr butane – 722-torr air (152 torr O₂) mixture can be represented as



assuming that CO and H₂ are products of incomplete combustion.

It is obvious that the initial pressure spike that accompanied ignition should subside as the temperature falls and the water vapor condenses. When the temperature returns to its initial value and the water condenses, the final pressure is identical to the initial pressure plus the equilibrium vapor pressure of water at room temperature.

The pressures of the agents required to inert the butane-air mixtures (essentially zero pressure increase upon ignition) along with the pressure increases associated with smaller agent concentrations were determined. The data for the 38-torr butane mixture are presented in Table 3.

It is recognized that many of the chemical compounds used in the inerting experiments have the potential to form significant quantities of HF when exposed to a flame environment. Analysis for HF was carried out for mixtures in 20-liter chamber after some of the inerting experiments. Concentrations of HF were determined in parts per million and a calculation was made to show the percent of agent molecules required to yield one HF each in order to obtain the amount of HF found. Data for the 30-torr butane mixture with HF analyses are given in Tables 4–7, including data on the percent of agent molecules yielding an HF product molecule, assuming only one HF comes from one agent molecule. The values in the last three columns of Tables 4–7 are averages of from 1–6 data points.

Table 3. Agent Concentration Required to Inert a
38-mm Butane-Air Mixture at 1 Atmosphere

Agent	Percent Required for Zero Pressure Increase
Perfluoroethyl Iodide	4.38
Halon 1301	4.49
Perfluoroheptane	4.66
Perfluoro - 2 - butyltetrahydrofuran	4.70
Perfluorohexane	4.75
Perfluoro (methylcyclohexane)	5.60
FE 232	6.78
Perfluorobutane	7.90
2 - Bromo - 1,1 - difluoroethylene	9.32

The pressure spike accompanying ignition is given in kPa, and pounds per square inch (psi). Therefore, ΔP in kPa can be converted to ΔP in torr by multiplying kPa in the last column of Tables 4, 5, 6, and 7 by 7.6.

4. DISCUSSION

4.1 HF. Tables 4, 5, 6, and 7 show the calculated percent of agent molecules which yielded an HF molecule during the inertion experiments. The percent of agent molecules yielding an HF is an interesting concept, since it demonstrates that while the total amount of HF formed may be increasing, it is possible that the percent of agent molecules which yield an HF may actually be decreasing. The agent can become more efficient in its inerting role, even though the HF concentration may increase.

4.2 Halon 1301. Table 4 shows that when Halon 1301 is used in an inerting scenario, over 30% of the agent molecules can yield an HF product molecule. This occurs when the concentration of the

Table 4. Production of HF When Halon 1301 is Used as an Inerting Agent in a Butane-Air Mixture at 1 Atmosphere

Butane (torr)	Halon 1301 (torr)	Halon 1301 (%)	HF (ppm)	Halon 1301 Molecules Yielding An HF (%)	ΔP (kPa) (psi)	
30	10	1.3	2,250	17.1	571	84
30	20	2.6	4,620	17.6	570	84
30	30	3.9	12,364	31.3	480	71
30	40	5.3	10,270	19.5	224	33
30	50	6.6	< 51	<0.1	3	0.5
30	60	7.9	< 51	<0.1	0	0
30	70	9.2	73	<0.1	0	0

Table 5. Production of HF When Perfluorobutane is Used as an Inerting Agent in a Butane-Air Mixture at 1 Atmosphere

Butane (torr)	PFB (torr)	PFB (%)	HF (ppm)	PFB Molecules Yielding An HF (%)	ΔP (kPa) (psi)	
30	10	1.3	2,440	18.5	575	84.5
30	20	2.6	7,469	28.4	560	82.3
30	30	3.9	11,227	28.4	526	77.3
30	40	5.3	7,416	14.1	342	50.2
30	50	6.6	6,360	9.7	61	9
30	60	7.9	235	0.3	0	0

Halon 1301 is high enough (3.9% Halon 1301) to seriously affect combustion, but not high enough to actually inert the mixture. At low concentrations of Halon 1301 (1.3%), the mixture appears to explode normally. Flame reaction is over in a short time. There is little time for Halon 1301 to interact with the flame; therefore, only a relatively small (17.1) percent of the agent molecules yield an HF.

Table 6. Production of HF When Perfluoroethyl Iodide is Used as an Inerting Agent in a Butane-Air Mixture at 1 Atmosphere

Butane (torr)	PFEI (torr)	PFEI (%)	HF (ppm)	PFEI Molecules Yielding An HF (%)	ΔP	
					(kPa)	(psi)
30	20	2.6	8,068	30.7	382	56.2
30	25	3.3	7,089	21.6	222	32.6
30	30	3.9	2,883	7.3	61	8.8
30	40	5.3	1,708	3.2	17	2.5
30	50	6.6	684	1.0	0	0

Table 7. Production of HF When Perfluoromethyl Iodide is Used as an Inerting Agent in a Butane-Air Mixture at 1 Atmosphere

Butane (torr)	PFMI (torr)	PFMI (%)	HF (ppm)	PFMI Molecules Yielding An HF (%)	ΔP	
					(kPa)	(psi)
30	20	2.6	< 51	0.2	558	82
30	25	2.6	3,230	10.0	567	83.5
30	30	3.9	4,032	10.2	406	59.7
30	40	5.3	1,470	2.8	149	21.9
30	50	6.6	1,175	1.8	70	10.3
30	60	7.9	206	0.3	3	0.5

At high concentrations of Halon 1301 (5.3%), the agent has a strong inerting ability. Only weak, although prolonged, combustion occurs. Therefore, a relatively small percentage (19.5) of the halon molecules produce an HF molecule in the weak flame zone.

In the mid-range of Halon 1301 concentrations, there is not enough agent to inert the system, yet there is enough to prolong the time of strong combustion, allowing a great deal of interaction of the Halon 1301 and free radicals in the flame zone.

4.3 Perfluorobutane. Table 5 shows a qualitatively similar trend with perfluorobutane as was observed with the halon. At low concentrations of perfluorobutane (3.9%), as much or even more HF is produced, compared to the halon. This is because there is not enough agent present to have a serious effect on the combustion process. However, there are more fluorine atoms available per agent molecule leading to more HF formation.

At the high end of agent concentration (over 6.6%) the perfluorobutane, which functions by a heat-absorbing mechanism, is able to inert the mixture—actually preventing flame. This virtually eliminates any HF formations.

In the mid-range of concentrations, the perfluorobutane produces less HF than the halon. This is probably due to the heat-absorbing agent lowering the flame temperature and concentration of free radicals.

4.4 Perfluoroethyl Iodide. Table 6 gives the results of the inerting experiments with perfluoroethyl iodide. At the low end of the agent concentration (3.3% or less), there is insufficient agent to seriously affect combustion. Production of HF is as high as with perfluorobutane. At the high end of concentration (approximately 5.3%), perfluoroethyl iodide is more effective than the heat-absorbing agent, perfluorobutane, and much more effective than the chemical agent, Halon 1301. In the mid-range of agent concentration, the perfluoroethyl iodide is also more effective than either of the two other agents.

The perfluoroethyl iodide appears to be acting like a superior heat-absorbing agent; but, in an obvious comparison to Halon 1301, it is predicted to be a chemical agent, with the iodine atoms reacting with free radicals in a fashion similar to bromine atoms of Halon 1301 reacting with free radicals(5). Thus, in the case of perfluoroethyl iodide,





adding (8), (9), and (10) gives



The HI, formed from C_2F_5I in a flame, should cause the catalytic combination to hydrogen atoms into H_2 . While the chemical action of C_2F_5I in a flame is probably correct, there may also be a mode of operation of C_2F_5I as a heat-absorbing agent. It is possible that the weak carbon-to-iodine chemical bond can be broken at a low enough temperature to act as a heat sink under incipient ignition conditions.



$\Delta H = + 57$ kcal/mole, or less(6) (Masterton and Slovinski 1977).

If this heat sink concept is correct, perfluoroethyl iodide may be able to act as both a good inerting agent and a good fire-extinguishing agent.

4.5 Perfluoromethyl Iodide. Table 7 gives the results of the inerting experiments using perfluoromethyl iodide. Up to and including 25 torr, the agent is not effective in inerting the butane air mixtures. The pressure pulse associated with ignition are quite high with a high flame spread. Little HF is formed under these conditions.

At 30 torr and above, perfluoromethyl iodide is more effective. Pressure pulses diminish with increasing agent pressure. Interestingly, the percent of agent molecules yielding an HF molecule is never high, reaching a maximum of 10.2% at 30 torr. This agent is less effective than perfluoroethyl iodide at this concentration, but more effective than Halon 1301 and perfluorobutane at the same concentrations.

At higher concentrations (50 torr and above), perfluoromethyl iodide is less effective than either Halon 1301 or perfluoroethyl iodide. All in all, perfluoromethyl iodide appears to be approximately as effective as Halon 1301 as an inerting agent, but not as good as perfluoroethyl iodide.

An interesting observation is that when analyzing for HF, a yellow powder frequently formed in the final solution (after 10 ml of the collection solution was dissolved in 90 ml of the acetate buffer). It was also sometimes observed in the glass lines of the gas washing bottle. It was even observed on the inner walls of the 20-liter chamber. However, it was never observed when using perfluoroethyl iodide.

No analysis of the yellow solid was attempted, but it was speculated that it could be iodine. Often, with precipitated solids, the color is due more to particle size than to the nature of the solid.

5. CONCLUSIONS

5.1 Halon 1301 and Perfluorobutane. Inerting experiments with Halon 1301, an agent which extinguishes fire primarily by a chemical mechanism, and perfluorobutane, an agent which functions primarily by a heat extraction mechanism showed that:

- (1) Neither type of agent produced much HF if the agent is used in such small quantities that it has little affect of the combustion of a premixed fuel-air system. There is little time for a fluorine atom to be extracted from the agent molecule, since the flame transverses the mixture at normal flame speed. This result might not hold if a supply of liquid or solid fuel were present to prolong combustion.
- (2) When used in large amounts, the heat-absorbing agent quenches flame rapidly, giving little HF, even when used in concentrations large enough to quench the flame.
- (3) Both types of agents produce excessive amounts of HF if used in amounts large enough to slow down combustion, but not large enough to quench the flame. The prolonged combustion produces much more HF from both types of agents. The time the agent spends in the flame zone is apparently very important in determining the amount of HF produced.

5.2 Perfluoroethyl Iodide and Perfluoromethyl Iodide. Inerting experiments using perfluoroethyl iodide and perfluoromethyl iodide showed that:

- (1) In the case of perfluoroethyl iodide, significant amounts of HF were found only when the concentration of the agent was so small that flame quenching was not accomplished.

However, this occurred only at low agent concentration, so that the total amount of HF produced was not great. At higher concentrations, the inerting effect from perfluoroethyl iodide is significant and prevents the formation of large amounts of HF. The low bond strength of the carbon-to-iodine bond provides a heat sink at relatively low temperatures, hindering the ignition process.

- (2) Perfluoroethyl iodide is much better suited to the role of inerting agent than either perfluorobutane or Halon 1301.
- (3) Perfluoromethyl iodide is approximately as effective as Halon 1301 as an inerting agent for a butane-air mixture.
- (4) Perfluoromethyl iodide is not as effective as perfluoroethyl iodide as an inerting agent but superior to perfluorobutane for inerting a butane-air mixture.

5.3 General. As is generally recommended in fire suppression scenarios, the best course of action is to use sufficient agent to extinguish the incipient fire as quickly as possible. When there is the possibility of the formation of toxic by-products from the fire extinguishing agent, it becomes even more important to quench the fire immediately or, at least, to allow only the minimum possible amount of chemical reaction to take place. The agents tested, all of which contain fluorines, produced the least amount of HF when large amounts of the agents were used and the combustion processes were quenched at the ignition stage.

There is a practical method of premixing a fire extinguishing agent with a fuel spray in a combat scenario. If the fuel cell is surrounded by a jacket of fire extinguishing agent, as described in a previous ARL report (Finnerty and Dehn 1994), the agent will be released with the fuel spray when the cell is attacked by a weapon. The agent and fuel are mixed before ignition occurs. The jacketed fuel cell was shown to be an effective method of preventing ignition of fuel that sprayed out of ruptured fuel cells.

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6. REFERENCES

- Finnerty, A. E., and J. T. Dehn. "Alternative Approaches to Fuel-Fire Protection for Combat Vehicles." ARL-TR-377, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, April 1994.
- Masterton, W. L., and E. J. Slowinski. Chemical Principles, Philadelphia: W. B. Saundins Co., 1977.
- Purdue Research Foundation and Department of Chemistry. "Final Report On Fire Extinguishing Agents for the Period September 11, 1947 to June 30, 1950." Purdue University, West Lafayette, IN, July 1950.
- Sheinson, R. S., H. G. Eaton, B. H. Black, R. Brown, H. Burchell, A. Maranghides, C. Mitchell, G. Salmon, and W. D. Smith. "Halon 1301, Replacement Flooding Fire Testing, Intermediate Scale." Proceedings of the Halon Options Technical Working Conference, pp. 43-53, Albuquerque, NM, May 3-5, 1994.
- Sheinson, R. S. "Halon Alternatives Extinguishment Pathways." Proceedings of the Halon Alternatives Technical Working Conference, Albuquerque, NM, pp. 71-82, April 30-May 1, 1991.
- U.S. House of Representatives. Congressional Record - House, H13177-H13184, Clean Air Act Amendment, Title VI - Stratospheric Ozone Protection, Washington, DC, October 26, 1990.

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